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CHLORINATION AND CHLORAMINE[1]

By Joseph Race

The studies reported in this paper are a continuation of those recorded in last year's JOURNAL (vol. 3, 1916, 439–449) and constitute a partial attempt to place water chlorination on a scientific basis. Until comparatively recently the data that we possessed were a disconnected mass of empirically established facts, and it is a regrettable feature that although it is on this continent that the *art* of chlorination has progressed the most rapidly, it is in Europe, under the stimulus of war, that it is being developed as a *science*. As chlorination becomes more general it becomes increasingly evident that our stock of information regarding the conditions that tend to successful results is very meagre, and that the dosage is largely determined by the trial and error method. We are also lamentably ignorant as to the reason why some waters have but very small margins between the dose required for satisfactory purification and that which causes complaints as to tastes and odors, while others have much greater ones and can easily absorb slight excesses of the sterilizing agent. Complaints that arise in this way are often ascribed to auto-suggestion by water works and health officials, but they are too often based upon solid fact to be disposed of in this manner, and the time and energy that have been devoted to deluding the public might much better have been spent in improving present methods and so eliminating the cause for complaints. Chlorination is such a cheap and simple process that it is often considered the *ultima thule* of chemical sterilization, but there is no reason to doubt that the present methods will be modified and considerably improved. A simple modification that has yielded good results with some waters will be described later, but before treating that in detail a few general factors will be considered. In the last paper, the author gave results showing the effect of time, mechanical admixture, temperature, and organic matter upon chlorination by bleach and also the relative viability of various types of B. coli to chlorine. In the present paper the effect of acids, alkalies, and salts will be discussed and a new explanation given of the *modus operandi* of chlorination.

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[1] Read before the Chemical and Bacteriological Section of the Richmond Convention, May 10, 1917.

All the experiments described below were made with the raw Ottawa river water, the general characteristics of which are as follows.

	parts per million
Free ammonia	0.005–0.015
Albuminoid ammonia	0.088–0.110
Chlorine	1.5 –2.5
Nitrites	Traces
Nitrates	0.045–0.080
Oxygen absorbed in 30 minutes at 100°C	9.0 –11.0
Alkalinity	25.0 –35.0
Free carbonic acid	0.66 – 1.32

Approximately 10 parts per million of calcium and magnesium sulphates and 0.5 parts per million of iron are usually present in addition to the bicarbonates and chlorides. The turbidity and color are recorded separately for each experiment.

The bacteriological experiments were made by adding the various chemicals to the water, contained in glass bottles, after seeding with a pure culture of B. coli and plating out 10 cc. after the contact indicated in the tables; 40 cc. rebipelagar (neutral red lactose bile salt agar) were added to the water and the plates incubated for twenty-four hours at 37°C.; the characteristic red colonies produced by B. coli were then counted and recorded. The results obtained are recorded in table 1.

Chlorides. The effect of small quantities of sodium chloride (up to 10 parts per million) is apparently very limited, but larger amounts tend to increase the velocity of the germicidal action of the hypochlorite. Sodium chloride itself has no effect on the viability of B. coli during the period covered, viz., five hours (experiments 1, 2, and 3).

Caustic potash. In quantities up to approximately 5 parts per million caustic potash has but little effect. At 5 to 10 parts per million the velocity of the germicidal action is materially reduced but when higher amounts are present the germicidal action of the alkali itself begins to take effect and may entirely nullify the retarding effect on the hypochlorite (experiments 4, 5, and 6).

TABLE 1

Effect of different quantities of several chemicals on the bacterial content of raw Ottawa River water. Results are B. coli per 10 cc.

EXPERIMENT NO.	AVAILABLE CHLORINE	ADDED CHEMICAL	PHYSICAL CONDITIONS		CONTACT PERIOD										
			Color	Turbidity	Nil	10 mins.	30 mins.	1 hour	1½ hours	2 hours	3½ hours	4 hours	5 hours	6 hours	24 hours
	p. p. m.	p. p. m.													
1	0.40	Sodium chloride													
		Nil	40	4	143			97		35	3		0		
		1.0						97		37	6		0		
		10.0						88		35	7		1		
		90.0						75		17	2		0		
2	0.40	Sodium chloride													
		1.0	40	10	133			94		46	15		4		
		5.0						103		37	13		3		
		10.0						92		43	12		5		
		20.0						88		39	6		0		
3	Chlorine absent	Sodium chloride													
		Nil	40	60	214			209		205	206		202		
		10.0						208		198	204		200		
		50.0						201		203	206		214		
		90.0						208		204	208		216		
4	0.40	Caustic potash													
		Nil	40	4	258	155		131				0		0	0
		0.74				160		118				0		0	0
		7.4				150		118				60		46	0
		37.0				158		48				0		0	0
5	0.40	Caustic potash													
		0.74	40	4	185			75		40		0			
		3.7						112		90		0			
		7.4						85		64		63			
		18.5						80		43		44			
6	Chlorine absent	Caustic potash													
		Nil	40	4	146			150				160		145	95
		7.4						126				140		128	87
		37.0						129				130		121	34
		74.0						131				124		90	0

TABLE 1—*Continued*

EXPERIMENT NO.	AVAILABLE CHLORINE	ADDED CHEMICAL	PHYSICAL CONDITIONS		CONTACT PERIOD										
			Color	Turbidity	Nil	10 mins.	30 mins.	1 hour	1½ hours	2 hours	3½ hours	4 hours	5 hours	6 hours	24 hours
	p. p. m.	*p. p. m.*													
7	0.40	Sulphuric acid													
		Nil	40	4	80			51		25	7		3		
		1.6						45		20	4		0		
		6.5						35		15	1		0		
		16.3						17		3	0		0		
8	Chlorine absent	Sulphuric acid													
		Nil	40	50	285			282		287	285		282		
		6.5						280		282	262		240		
		16.2						285		285	255		220		
		32.5						290		275	222		190		
9		Carbonic acid													
	0.35	Nil	40	4	197	205	141	87							0
	0.35	Saturated				90	70	50							0
10	0.35	Sodium carbonate													
		Nil	30	15	70		44	40	37				2		
		5.0					45	38	36				1		
		25.0					52	42	38				11		
		90.0					56	44	38				9		
11	0.35	Sodium bicarbonate													
		Nil	38	9	140		85	82	73			63			
		5.0					93	75	68			60			
		25.0					90	80	65			60			
		90.0					93	73	35			28			
12	0.35	Effect of light													
		In bright sunlight	38	9	215		130	122	61		0				
		In dark cupboard					145	136	130		32				

Acids. The bleach solution used in experiment 9 contained 0.01 per cent of available chlorine and was dissociated to the extent of 40 per cent. This was carbonated until hypochlorite was more than 95 per cent dissociated.

The results of experiments 7, 8, and 9 show that small amounts of acid, whether added as a strong mineral acid, or a weak acid such as carbonic acid, increase the velocity of the action in a marked manner. Sulphuric acid alone has a germicidal effect but insufficient to account for the observed effect of the addition of acid to hypochlorites.

COMPARISON OF VARIOUS SOURCES OF CHLORINE[2]

1. Bleach and chlorine gas. The results in experiment 13 show a slight difference in favor of the solution of chlorine gas, but it is so small as to be of no practical importance. A similar conclusion is reached by Avery (*Report of the Ontario Provincial Board of Health, 1914*) after a number of experiments with sewage-infected water. The general characteristics of the water used by Avery are very different to those of the Ottawa supply; the Toronto supply is much harder (alkalinity about 100) and contains no color. The results obtained in Ottawa and Hull are perhaps of more value than laboratory experiments. Both these cities take their supplies from the same river and from approximately the same location, and daily analyses extending over a period of years have proved that the raw water is the same in both cases. In Ottawa the water was treated with straight bleach and in Hull with liquid chlorine from a modern type of apparatus, both using the same dosage. When tap samples from the two cities were examined after the same contact period the results were practically identical. For a short period liquid chlorine was used in Ottawa and the results were very similar to those obtained with the same dosage of chlorine as bleach.

2. Bleach and electrolyzed salt. In experiment 14 there is a slight difference in favor of the electrolytic product but insufficient to be of practical significance. The electrolyzed salt solution was obtained from a large-sized Dayton cell and contained 13 pounds of salt per pound of available chlorine.

3. Bleach and ammonium hypochlorite. The ammonium hypochlorite used in experiment 15 was prepared by double decomposition of a solution of bleach by ammonium oxalate and removal of the calcium oxalate by centrifugalization. No excess of oxalate was present.

The abnormally high efficiency obtained with what was presuma-

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[2] See table 2.

TABLE 2

Comparison of various sources of chlorine. Results are B. coli per 10 cc.

EXPERIMENT NO.	AVAILABLE CHLORINE	SOURCE OF CHLORINE	AMMONIA	PHYSICAL CONDITIONS		CONTACT PERIOD											
				Color	Turbidity	Nil	10 mins.	30 mins.	45 mins.	1 hour	1¼ hours	1½ hours	2 hours	3½ hours	4 hours	24 hours	48 hours
	p.p. m.		*p.p.m.*														
13	0.4	Liquid chlorine		40	4	195	160			60					36	20	6
	0.4	Bleach					170			75					51	30	17
	0.5	Liquid chlorine					150			26					1	0	0
	0.5	Bleach					160			30					1	0	0
14	0.4	Bleach		40	4	182		130		66			3	0			
	0.4	Electrolyzed salt						115		60			1	0			
	0.6	Bleach						30		1			0	0			
	0.6	Electrolyzed salt						25		0			0	0			
15	0.3	Bleach		40	4	440	380			320					180	26	1
	0.3	Ammonium hypochlorite				280	80			4					0	0	0
	0.4	Bleach				440	300			218					112	6	1
	0.4	Ammonium hypochlorite				280	30			0					0	0	0
	0.5	Bleach				440	290			191					59	2	0
	0.5	Ammonium hypochlorite				280	10			0					0	0	0
16	0.35	Electrolytic hypochlorite	Nil	25	45	58		31		27		20		1			
	0.10		0.05					41		19		7		0			
	0.20		0.10					26		0		0		0			
	0.35		0.15					0		0		0		0			
17	Nil	Bleach	Nil	40	6	365	370			360					380	330	260
	0.4		Nil				240			118					9	8	4
	0.6		Nil				160			44					1	0	0
	0.2		0.10				280			24					2	0	0
	0.3		0.15				210			7					0	0	0
	0.4		0.20				115			3					0	0	0
18	0.2	Bleach	Nil	41	5	145	133			113					110	110	
	0.5		Nil				114			24					7	0	
	0.2		0.05				72			7					3	0	
	0.2		0.10				76			4					0	0	
	0.2		0.20				81			6					1	0	

TABLE 2—*Continued*

EXPERIMENT NO.	AVAILABLE CHLORINE	SOURCE OF CHLORINE	AMMONIA	PHYSICAL CONDITIONS		CONTACT PERIOD											
				Color	Turbidity	Nil	10 mins.	30 mins.	45 mins.	1 hour	1¼ hours	1½ hours	2 hours	3½ hours	4 hours	24 hours	48 hours
	p.p. m.		*p.p. m,*														
19	0.2	Bleach	Nil	40	8	173			165		155		140		130		
	0.2		0.025						150		120		4		0		
	0.2		0.050						140		112		4		0		
	0.2		0.100						135		105		3		0		
20	Nil		0.17	40	8	215				212					218		
	Nil		0.35							215					212		
	Nil		5.00							210					205		
21	0.20	Liquid chlorine	Nil	40	5	130	135			130					120	120	
	0.20		0.05				140			130					112	145	
	0.20		0.10				130			128					110	160	
	0.20		0.20				135			120					105	170	

bly ammonium hypochlorite was subsequently confirmed on several occasions. If the velocity of the germicidal action is calculated on the results obtained with 0.3 part per million of available chlorine the following values are obtained by means of the formula

$$v = \frac{\log \frac{N_1}{N_2}}{t_2 - t_1}, \text{ when } t_1 = 0.$$

t_2	VELOCITY COEFFICIENT OF		RATIO $\frac{\text{AMMONIUM SALT}}{\text{CALCIUM SALT}}$
	Calcium salt	Ammonium salt	
hours			
1	0.138	1.841	13.3
4	0.099	+0.612	+6.2

These figures indicate very clearly the marked increase in the velocity shown by the ammonium salt. From a consideration of the chemical formula of ammonium hypochlorite it appeared probable that it would be exceedingly unstable and decompose into chloramine and water according to the equation: $NH_4OCl = NH_2Cl + H_2O$. Chloramine has previously been found to have a carbolic coefficient of 6.6 as compared with 2.2 for chlorine. (S. Rideal, *Jour. Roy. San. Inst.*, 1910, 31, 33–45.) A dilute solution of pure chloramine can be prepared by Raschig's method (*Chem. Zeit.*, 1907, 31, 926) in which dilute solutions of bleach and ammonia are mixed in such proportions that the anhydrous ammonia is equivalent to the available chlorine (approximately two parts by weight of chlorine to one part by weight of ammonia). During the addition of the ammonia the solution of bleach should be surrounded by a freezing mixture and the mixture kept as cool as possible until the evolution of gas has ceased. The solution is then saturated with zinc chloride and magma distilled under reduced pressure. The distillate is a dilute solution of pure chloramine. Rideal (loc. cit.) found that mixtures of electrolytic hyphochlorite and ammonia produce chloramine and this is confirmed by the results given in experiment 16. The effect of adding ammonia to bleach solutions is shown in experiment 17. If the results are calculated by means of the formula given on page 69, the following velocity coefficients are obtained, t being expressed in hours.

t_2-t_1	STRAIGHT BLEACH		BLEACH PLUS AMMONIA,		
	Available chlorine parts per million				
	0.40	0.60	0.20	0.30	0.40
0.166 (10 minutes)	1.092	2.149	0.691	1.440	3.369
1.0 (1 hour)	0.490	0.919	1.182	1.747	2.085

Over a period of one hour the velocity coefficient of 0.20 part per million of chlorine plus an equivalent of ammonia is greater than that of 0.60 part per million of chlorine without ammonia.

The next step was to determine the most efficient ratio of chlorine to ammonia. The results are given in experiments 18 and 19. Experiment 18 shows that there is apparently but little difference in the results when the ammonia is present in amounts that lie between one half the equivalent of the chlorine and double the equivalent. The tendency of amounts larger than the equivalent is an adverse one, due, possibly, to the production of hydrazine or ammonium chloride. Experiment 19 shows that when the ammonia is as low as one quarter the equivalent of the chlorine, the velocity of the reaction is practically as great as when an equivalent is used. No satisfactory explanation of this can be advanced at present by the author, but in corroboration of the results the figures in table 3 are given, which show the rate of absorption of available chlorine for various ratios of chlorine and ammonia.

Similar indications were given by testing the bleaching power of solutions containing various ratios of chlorine to ammonia. All the laboratory experiments that have been made, indicate that the effect of the ammonia is altogether out of proportion to its amount.

TABLE 3

Rate of absorption of chlorine

10 parts per million of available chlorine added. Temperature, 65°F.

RATIO OF $\frac{\text{CHLORINE}}{\text{AMMONIA}}$ BY WEIGHT	PERCENTAGE OF ORIGINAL FOUND AFTER		
	10 minutes	4 hours	20 hours
Infinity. (ammonia absent)	66.8	40.0	28.1
8 : 1	83.2	77.8	67.3
4 : 1	97.2	94.7	88.5
2.7 : 1	98.3	96.5	92.8
2 : 1	99.8	98.2	96.2

Ratio of 8 : 1 by weight = ratio of 4 : 1 in equivalents.

EVIDENCE OF THE FORMATION OF CHLORAMINE

So far as the author is aware, there is no specific test for chloramine, and although the evidence regarding the formation of this substance from ammonia and hypochlorites or hypochlorous acid, when present in equivalent amounts in dilute solution, is purely circumstantial it must be regarded as fairly conclusive. It has been suggested that the effect of the ammonia is to accelerate or intensify the oxidizing action of the hypochlorite, but this view is contrary to the evidence available. If the oxidizing action were intensified, the rate of absorption of available chlorine by waters containing appreciable amounts of organic matter would be more rapid after the addition of an equivalent of ammonia, but the data at the top of the next page show that the converse holds true.

CONTACT PERIOD	ABSORPTION OF AVAILABLE CHLORINE AT 63° C.	
	Chlorine as bleach	Chlorine as chloramine
minutes		
0	10.00	9.98
5	6.50	9.98
10	5.91	9.90
20	5.18	9.90
40	4.47	9.84
60	3.96	9.88
80	3.65	9.84
1200		9.68

The effect of the ammonia in this case was to reduce the rate of absorption to a negligible amount; the amount of chlorine absorbed in eighty minutes after the addition of ammonia is so small as to be almost within the limit of experimental error.

Another method of estimating the effect of the ammonia on the oxidizing power of hypochlorites is by determining the bleaching action on dyestuffs. Indigo, as indigo carmine, is very suitable for this purpose, as it is first oxidized to isatin, a colorless compound, which is then converted to yellow chlorisatin by the action of chlorine. In one experiment it was found that 10 cc. of a bleach solution containing 1 mgm. of available chlorine, after the addition of 10 cc. of warm 25 per cent sulphuric acid, decolorized 13.0 cc. of a weak indigo carmine solution. When an equivalent of ammonia was first added to the bleach solution only 0.2 to 0.3 cc. was required to produce a blue color that was permanent for several hours. Similar results have been reported by Rideal for mixtures of sodium hypochlorite and ammonia and prove conclusively that the addition of the ammonia destroys the bleaching or oxidizing effect of hypochlorites.

Although chloramine has no oxidizing value, it still retains the property of displacing iodine from potassium iodide and consequently gives the usual starch iodide reaction. The chlorine can also be precipitated by silver nitrate and the ammonia determined by the colorimetric method with Nessler's reagent.

Chloramine is very stable in *very* dilute solution and no loss of nitrogen or available chlorine occurs in mixing very dilute solutions of hypochlorites and ammonia, but when the solutions are more concentrated a serious loss of available chlorine takes place on standing. This is especially marked if there is a local excess of ammonia, such as occurs on the addition of ammonia fort. A bleach solution containing 0.63 per cent of available chlorine lost 14 per cent of available chlorine in twenty hours, and 24 per cent in twenty-four hours, after the addition of dilute ammonia; when ammonia fort was used, the solution lost 89 per cent of its available chlorine in a few hours. On adding strong ammonia to bleach solutions a white precipitate of hydrate of lime is thrown down and a rapid evolution of nitrogen occurs. According to Raschig two competing reactions take place when the ammonia is in excess.

(1) $NH_2Cl + NH_3 = N_2H_4.HCl$ (Hydrazine hydrochloride) and
(2) $3NH_2Cl + 2NH_3 = N_2 + 3NH_4Cl$
When the excess of ammonia is large the second reaction predominates and the yield of nitrogen gas is almost quantitively proportional to the available chlorine in the solution.

Hydrazine has a carbolic coefficient of 0.24 (Rideal) and ammonium chloride has no germicidal action so that if ammonia is to be efficiently employed dilute solutions must be used and a local excess of ammonia avoided.

It appeared possible that chloramine might be prepared by the electrolysis of ammonium chloride but, up to the present, efforts in this direction have not been successful. When warm concentrated solutions are used, nitrogen trichloride (NCl_3) is formed. This is a heavy oily substance that is extremely unstable and highly explosive. When dilute cold solutions are used, a small amount of available chlorine is produced but, owing to secondary reactions which result in the formation of free acid, the concentration does not increase. This chlorine is not of the nature of chloramine, because such solutions have a decided bleaching action on dyestuffs. When the production of acid is prevented by the addition of ammonia, hydrazine is apparently produced. Another compound of ammonia and chlorine is possible, viz., $NHCl_2$, dichloramine, but its method of preparation and properties are apparently unknown.

The increased germicidal effect produced by adding ammonia to hypochlorites naturally suggests a similar mixture with a solution of chlorine gas but under the usual conditions this apparently has no abnormal value. A typical example of this is shown in experiment 21.

The results are explained by the fact that a solution of chlorine gas in water does not form hypochlorous acid and is consequently unable to produce ammonium hypochlorite and chloramine. The addition of ammonia to solutions of chlorine gas almost entirely destroys both the oxidizing action and the germicidal action by the formation of inert ammonium chloride. In experiment 21 the effect of this salt is seen in the twenty-four hour results, which show that an aftergrowth of B. coli had occurred which was somewhat proportional to the amount of ammonia added.

MODUS OPERANDI OF CHLORINE DISINFECTION

When bleaching powder is the source of the chlorine the usual method of representing the reactions is by the following equations, in which the nascent oxygen is regarded as the active germicidal agent

$$2CaOCl_2 = CaCl_2 + Ca\,(OCl)_2$$

$$Ca\,(OCl)_2 + H_2O + CO_2 = CaCO_3 + 2HCl + O_2$$

$$\text{or}\quad CaCl_2 + H_2O + O_2$$

Bleaching powder containing 38 per cent of available chlorine has the composition represented by the formula $4CaOCl_2 . 2Ca(OH)_2 . 5H_2O$. When temperature conditions are favorable the chlorine content can be increased to 40 and 42 per cent, but such compounds are not so stable as the one represented by the above formula, which contains approximately 20 per cent of excess hydrate of lime. The stability of bleach solutions depends upon this excess of base (Griffen and Hedallen, *J. Soc. Chem. Ind.*, 1915, 34, 530–532) and although magnesia can be partially substituted for the excess lime a minimum of 5 per cent of lime is required to ensure stability.

Instead of a definite chemical compound, bleach should be regarded as the solid phase of a three-component system which is in equilibrium only under the conditions of temperature and pressure obtaining during its manufacture. Although many of the alterations in equilibrium are of importance, the one of chief interest in disinfection is that produced by the addition of water. The best method of representing this alteration is by the equation $2CaOCl_2 + 2H_2O \rightleftarrows CaCl_2 + Ca(OH)_2 + 2HClO$. which accords with the fact that on distilling a solution of bleach with water or a dilute weak acid such as boric acid, a solution of hypochlorous acid is obtained. It also gives a clear explanation of the fact that ordinary bleach solutions give a higher chlorine content after acidification. It has been stated that when hydrochloric acid is employed the increase in the available chlorine is derived from the chlorine in the calcium chloride, but this never occurs under ordinary conditions. Weak acids, such as acetic or carbonic acids, will give just as high results as hydrochloric acid. The effect of acids is to remove the hydrate of lime from the right hand portion of the equation and so enable the reaction to proceed entirely in that direction. According to the law of mass action a similar result should be obtained by increasing the molecules of water relative to those of bleach. The author carried out this idea with a 2 per cent bleach solution with the results given in table 4.

The above figures only hold for the particular sample used; other samples containing different excesses of base would give different results.

These results are in accord with the above hypothesis and also show that bleach solutions are entirely dissociated or hydrolyzed at the dilutions used in water and sewage purification, provided the liquid does not contain substances that impede the dissociation. The dissociation can be reduced by the addition of lime water, caustic alkali or normal carbonate and increased by the addition of any acid that will neutralize and so remove calcium hydrate from the reaction. The effect of chlorides is anomalous and no apparent explanation of their action can be given. The addition of small quantities of sodium chloride (0.1 per cent) increases the dissociation of bleach solutions but much larger quantities tend to have the opposite effect. Bicarbonates increase the dissociation. These observed chemical effects are entirely in agreement with the bacteriological results given in table 1.

TABLE 4

Dilution of bleach

PERCENTAGE OF BLEACH IN SOLUTION	$\frac{\text{DIRECT TITRATION} \times 100}{\text{ACID TITRATION}}$
2.0	30.8
0.2	34.3
0.1	41.8
0.02	67.5
0.002	100.0

A phenomenon of more scientific interest than of practical importance has been noted by Breteau (*J. Phar. Chem.*, 1915, 12, 248) who found that alkaline solutions of sodium hypochlorite containing 0.94 per cent of available chlorine lost 3.8 per cent of their titer on dilution with 80 volumes of water; also that this loss was increased by the addition of small quantities of salt (sodium chloride) and more so by carbonates and bicarbonates. This has been found by the author to hold true for bleach solutions and that the loss increased on standing. It must be assumed that, in dilute solution and in the presence of light, there is a tendency for the reaction $2HClO = 2HCl + O_2$ to occur with loss of available chlorine. Carbonates and bicarbonates would increase the velocity of this reaction, but there is no apparent reason why common salt should have a similar effect.

Sodium hypochlorite is probably hydrolyzed in dilute solution in a manner similar to bleach, $2NaOCl = NaCl + NaOH + HClO$. For solutions containing equal amounts of available chlorine, NaOCl is more dissociated than bleach because of the absence of an excess of base and this, together with the excess of salt, accounts for the slightly higher germicidal velocity obtained with electrolytic hypochlorite. The experience of pulp mills with bleach and electrolytic hypochlorite confirms this; the latter is a much quicker bleaching agent than bleach and it is often so rapid as to make it desirable to reduce the velocity by the addition of soda ash.

The effect of salts and carbonates on solutions of chlorine gas has not been investigated and it is very difficult to deduce them from theoretical considerations on account of the extremely limited ionization of chlorine even in dilute solution.

Both chloride gas and hypochlorite solutions have an oxidizing power equivalent to their chlorine content and both yield 16 parts of oxygen per 71 parts of available chlorine. When a solution of chlorine gas or a hypochlorite is added to water or sewage containing readily oxidizable matter an equivalent of chlorine is dissipated and removed from the sphere of action. This may take place in two ways (1) by the addition of chlorine similar to the oxidation of ferrous chloride to ferric chloride or (2) oxidation by means of nascent oxygen produced by decomposition of hypochlorous acid or by the reaction of chlorine and water. If the reaction took place along the lines of the first suggestion an organic chloro-compound would be obtained in which the chlorine may not react in the usual way with silver nitrate. When bleach is added to the Ottawa River water the whole of the chlorine can be titrated with silver nitrate even after the whole of the free chlorine has disappeared and it therefore seems probable that the oxidation proceeds in accordance with suggestion 2. There is no reason for assuming, however, that the germicidal action property of chlorine and hypochlorites is due to the production of nascent oxygen for it is well known that such active oxidizing agents as sodium, magnesium, and hydrogen peroxides have a much lower germicidal power than chlorine when compared on the basis of their oxygen equivalents. This is shown in table 5 in which a comparison is made between bleach and potassium permanganate.

In this experiment the chlorine is five times as active as potassium permanganate when calculated on their oxygen equivalents and this value would probably have been much higher if the water used had contained less organic matter. Hypochlorites have a much higher germicidal action than can be accounted for by their oxidizing ability and are still more active when their oxidizing activity is destroyed by the addition of ammonia. The germicidal activity must consequently be attributed to some other cause and it seems probable that chlorine and certain of its compounds exert a direct toxic effect on organisms.

TABLE 5

Bleach and potassium permanganate. Results are B. coli per 10 cc.

CONTACT PERIOD	BLEACH. AVAILABLE CHLORINE, 0.35 PARTS PER MILLION	POTASSIUM PERMANGANATE		
	Oxygen equivalent parts per million			
	0.08	0.133	0.266	0.40
Nil	140			
30 minutes	90	122	115	110
1 hour	68	115	100	80
1½ hours	63	108	95	75
4 hours	50	95	80	50

Dakin (*Comptes rend.*, 1915, 161, 150–153) from a study of his boricized solutions of hypochlorites in the treatment of infected wounds has attributed the persistent action to the formation of chloro-amines by the reaction of protein and amino acids with hypochlorites. In a later paper (Dakin and Cohen, *Brit. Med. Jour.*, 1915, ii, 318) he reported the examination of a number of chloramines and found that all substances containing the group: NCl were strongly antiseptic. One of these, paratoluenesulphochloramide, $CH_3.C_6H_4.SO_2.NNaCl$, has been placed on the market under the name of chloramine T and is being extensively used in Europe for the treatment of wounds infected with the gas-gangrene bacillus, B. perfringens. Dilute hypochlorite solutions contain hypochlorous acid and the latter either exerts a direct toxic effect on the organisms or indirectly so after the formation of chloroamines by reaction with the protein and amino acids. Compounds such as chloramine produced by the reaction of hypochlorous acid and ammonia, would by analogy be strongly antiseptic themselves and also exhibit a marked tendency to react with compounds to form others containing the group NCl. It is interesting to note that Cross and Bevan (*J. Soc. Chem. Ind.*, 1908, 28, 260) have shown that chloramines have a tendency to combine with nitrogenous molecules and to become fixed on cellulose. It is possible that the action of chlorine and chloramine is a cytolytic one but the toxic action is probably much greater than can be accounted for in this manner.

CHLORAMINE DISINFECTION IN PRACTICE

At the time when the very abnormal results were obtained with ammonium hypochlorite the discovery appeared to be only of scientific interest and especially so inasmuch as Rideal had attributed the obnoxious tastes and odors sometimes caused by chlorination to the formation of chloramines. During the winter of 1915–1916, however, the price of bleach advanced to extraordinary heights and the author then determined to try out the process on a practical scale for the purification of water. A subsidiary plant pumping about 200,000 imperial gallons per day was found to be available for this purpose and the chloramine process was substituted for the bleaching powder method previously in operation. This was commenced by the addition of pure ammonia fort, in the calculated amount, to the bleach solutions contained in barrels. The results were not what were anticipated and it was found that the bleach solutions as received in the laboratory were far below the strength calculated from the amount of dry bleach used. This experience was repeated on subsequent days and the deficiency was found to increase with increased amounts of ammonia. Solutions of similar strength were then used in the laboratory with similar losses and it was observed that on the addition of ammonia a copious evolution of gas occurred. This led up to the work reported on page 73 which showed that dilute solutions must be employed and prolonged contact avoided. Alterations were accordingly made in the plant and the bleach and ammonia were prepared in dilute solutions in separate vessels and only allowed to mix for a few seconds before delivery to the suction of the pumps. This method of application was instantaneously successful and results equal to those obtained in the laboratory were at one secured. The dosage was reduced until the bacteriological results were adversely affected and continued at values slightly in excess of this figure for some time to prove that the process was reliable.

The results obtained on the experimental plant, together with those obtained on the main plant, where 20,000,000 imperial gallons per day were treated with straight bleach, are given in the tables 6, 7, and 8. The two periods given are during the spring floods and that immediately preceding it. These represent the worst and the best water periods. The results in both cases are from samples which were examined approximately two hours after the application of the treatment.

The cost data are calculated on recent spot prices for bleach and ammonia (26° B) in the United States, but if the prevailing Canadian prices are substituted the chloramine process shows an even greater economy. The results were so satisfactory that the author recommended the adoption of this method for the main plant and

TABLE 6

Comparison of hypochlorite and chloramine treatment

Bacteriological results

1916	RAW WATER			TREATED WITH HYPOCHLORITE ALONE				TREATED WITH HYPOCHLORITE AND AMMONIA				
	Bacteria per cubic centimeter		B Coli Index per 100 cc.	Bacteria per cubic centimeter		B Coli Index per 100 cc.	Available chlorine parts per million	Bacteria per cubic centimeter		B Coli Index per 100 cc.	Available chlorine parts per million	Ammonia, parts per million
	Agar 1 day at 37°C.	Agar 3 days at 20°C.		Agar 1 day at 37°C.	Agar 3 days at 20°C.			Agar 1 day at 37°C.	Agar 3 days at 20°C.			
March 15–31...	44	238	35.7	4	12	<0.14	0.90	4	12	0.14	0.22	0.11
April 1–19......	3,099	14,408	195.5	32	56	0.50	1.10	33	246	0.74	0.25	0.13

TABLE 7

Percentage reduction

	HYPOCHLORITE ALONE				HYPOCHLORITE AND AMMONIA			
	Bacteria per cubic centimeter		B. coli index per 100 cubic centimeters	Available chlorine parts per million	Bacteria per cubic centimeter		B. coli index per 100 cubic centimeters	Available chlorine parts per million
	Agar 1 day at 37°C.	Agar 3 days at 20°C.			Agar 1 day at 37° C.	Agar 3 days at 20° C.		
March 15–31	90.9	95.8	99.9+	0.90	90.9	95.0	99.7	0.22
April 1–19	98.9	99.6	99.7	1.10	98.3	98.9	99.6	0.25

TABLE 8

Cost per million imperial gallons

	HYPOCHLORITE ALONE	HYPOCHLORITE AND AMMONIA
March 15–31	$1.12	$0.46
April 1–19	$1.26	$0.54

Calculated on Bleach at $3.80 per 100 pounds and aqua ammonia (26°B) at 5¾ cents per pound.

requested the permission of the local Board of Health to make the change. The matter was referred to the Provincial Board of Health who granted the request provided the chlorine dosage was not reduced below 0.60 parts per million for at least six months. The effect of this would have been to render the treatment more costly than the straight bleach process and consequently nothing further was done. Early in 1917 the Canadian manufacturers again raised the price of bleach, to $5.10 per 100 pounds, and the permission of the civic authorities was then obtained for the proposed change at the main plant where 20,000,000 imperial gallons per day were being treated with bleach. The ammonia used in this instance was commercial aqua ammonia (26°B) containing approximately 29 per cent of anhydrous ammonia. The material was first examined for the presence of such noxious substances as cyanides and found to be very satisfactory.

The chlorinating plant is situated in close proximity to the low-lift pumping station at the mouth of the intake pipe and at present (April, 1917) discharges a 0.6 per cent bleach solution through a 2-inch galvanized iron pipe to the pumping station, where it is divided up by means of a manifold system and discharged into the suctions of the pumps. The aqua ammonia is diluted in barrels to approximately 0.40 per cent strength and discharged through an orifice under constant head into the hypochlorite feed pipe as it enters the station. The dosage of bleach and ammonia is determined by the strength of the solutions and by the heads on their respective orifices; and the mixtures of the two is divided among the pumps by regulating the valves on the discharge manifold until the water from all the pumps gives the same intensity of reaction with starch and potassium iodide. The low-lift pumps discharge into a common header from which the intake pipe carries the water to the high-lift pumping station situated some 5200 feet away. Calculated on the average daily consumption of water, a contact period of approximately twenty-five minutes is obtained before the treated water reaches the distribution mains.

TABLE 9

1917	B. COLI PER 100 CC.		TURBIDITY	COLOR	DOSAGE. PARTS PER MILLION	
	Raw water	Tap samples			Chlorine	Ammonia
February	268	0.88	3	40	0.57	0.05
March 1–18	250	0.96	4	40	0.32	0.11
March 1–31	643	0.43	4	40	0.47	0.14
April 1–30	5,228	0.14	31	32	0.60	0.10

Early in February the change in the treatment was effected by gradually increasing the quantity of ammonia until a dosage of 0.12 parts per million was reached and constantly decreasing the dosage of bleach, which was formerly 0.93 parts per million of available chlorine. During this period the results were constantly controlled by numerous bacteriological examinations which showed that the results were very satisfactory. When the dosage had been reduced to 0.28 part per million of chlorine, the health authorities intervened, with the result that the dosage was instructed to be increased to the minimum recommended by the provincial authorities. This has so far prevented a thorough test being made of the capabilities of the chloramine process but some results have been obtained that are of interest. The average B. coli results are given in table 9 together with the physical data which show that the April period includes the spring flood period.

At the height of the flood period the water contained 80 parts per million of turbidity and 500 to 1000 B. coli per cubic centimeter yet satisfactory purification was obtained with 0.60 part per million of available chlorine and 0.13 part per million of ammonia. The tap samples at this time averaged 2.5 B. coli per 100 cc. The treated water taken on this day from Hull, where the same raw water is treated with 0.7 part per million of liquid chlorine, gave a B. coli index of 26.7 per 100 cc. and previous experience in Ottawa has shown that under similar physical and bacteriological conditions at least 1.5 parts per million were required to reduce the B. coli index to 2.0. It is very evident that, with normal turbidities of 4 to 8 and a B. coli index of 20 to 50 for the raw water, the 0.6 part per million of chlorine together with 0.10 of ammonia will provide a very generous margin of safety. Even at this excessive dosage the process is financially successful and is saving approximately $8 per day at the present time.

The addition of ammonia has caused no complaints to be made regarding tastes and odors. Chloramine itself has a pungent and penetrating odor that is somewhat similar to that of chlorine but as tastes and odors seem to be associated with the chlorine part of the compound, any method that reduces the chlorine dosage also reduces complaints. This is one of the most valuable features of the new process and one that should commend itself to those who have to treat waters that have small margins between the dosage required for satisfactory purification and that which causes complaints. The chloramine process can be most efficiently employed by using small doses and long contact periods but there is, of course an economical limit to the contact period in water works practice. Waters that are very free from oxidizable matter will probably not give the same relative efficiency with chloramine treatment as that shown by the Ottawa River and on the other hand higher ratios should be obtained with sewage and sewage effluents.